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LINEAR SWEEP VOLTAMMETRY OF ADSORBED NEUTRAL RED.(U)

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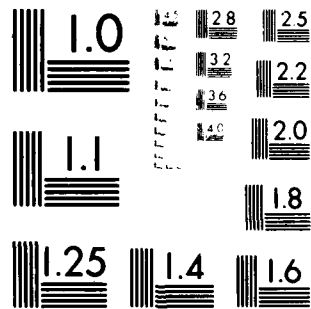
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Linear Sweep Voltammetry of Adsorbed Neutral Red

by

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ABSTRACT

The strong adsorption of neutral red on mercury causes its linear sweep voltammetry to be adsorption controlled over a wide range of conditions. At pH 4.5 or below, the surface coverage of DH^+ increases monotonically from 1 monolayer in $3 \times 10^{-7} M$ solution to ca 3 monolayers in $3 \times 10^{-4} M$ solution, and to a good approximation the monomeric, dimeric and tetrameric forms of the dye are adsorbed equally strongly. The morphology of the adsorption peak indicates that interactions between adsorbed molecules are substantial and that the nature of these interactions changes from moderately repulsive below pH 4 to strongly attractive above pH 6. Over this pH range the voltammograms of $2 \times 10^{-4} M$ dye narrow progressively and ultimately split into two extremely sharp peaks. The first of these corresponds to the single voltammetric peak observed for dilute dye solutions, whereas the second represents the reduction of an electrochemically distinguishable phase of adsorbed dye. Above pH 9 the isotherm for adsorption of D exhibits an abrupt increase when the bulk concentration exceeds the equilibrium solubility.

INTRODUCTION

Neutral red, an azine dye first synthesized by Witt [1], is widely used as a biological stain and a pH indicator, but little is known of its electrochemistry. In contrast to the much studied redox chemistry of the related thiazine dyes, the redox chemistry of neutral red has received little attention. The pioneering work of Clark and Perkins [2] showed that neutral red undergoes a potentiometrically reversible two-electron reduction to the leuco dye and established approximate acidity constants for both the dye and the leuco dye from equilibrium potential measurements. More recently, Bartels [3,4] estimated the acid dissociation constant of neutral red and the formation constants of the dimer and the tetramer of the acidic form of the dye. In an extensive systematic study of the effects of pH and the total dye concentration on the equilibrium potential of the dye-leuco dye couple, Nikolskii and coworkers [5-7] derived precise values for the two pK_a s of the leuco dye, the pK_a of neutral red and the formation constants of the dimer and the tetramer of the acidic form of the dye. Voltammetric study of neutral red appears to be limited to the report of Suzuki and Sawada [8], who studied its reduction from pH 1 to pH 6 using ac and dc polarography. The focus of their work was the second reduction step which follows the fast two-electron reduction to the leuco dye, and which they attributed to an irreversible reduction of a substance derived from leuco neutral red.

Structurally, neutral red closely resembles the thiazine dyes thionine and methylene blue, and in general one would

anticipate that its electrochemistry would be similar to that of these thiazine dyes. Of special interest is the strong adsorption of the thiazine dyes, [9-12], which suggests that the adsorption of neutral red would play a prominent role in its electrochemistry. We present here a detailed study of the adsorption of neutral red on mercury which emphasizes the interactions between adsorbate molecules and the nature of the resulting surface films.

EXPERIMENTAL

Linear sweep voltammetry was performed at sweep rates up to 0.2 V/s using a PAR Model 170 Electrochemistry System and at higher sweep rates using a PAR Model 173 potentiostat driven by a PAR Model 175 programmer and coupled to a Biomation 1010 waveform recorder. Positive feedback was used to compensate solution resistance as determined from the behavior of the Cd(II)/Cd(Hg) couple. The reference electrode was Ag/AgCl in saturated KCl, the potential of which was -0.042 V vs SCE and the working electrode was a Metrohm hanging mercury drop electrode. The supporting electrolyte was 0.1M KCl buffered with 0.01M phosphate, acetate or borate as appropriate, and all experiments were performed at $22.0 \pm 0.2^\circ\text{C}$ in a thermostated vessel. Surface coverages were estimated from voltammetric data by graphical integration.

Triply distilled water was used throughout and all chemicals were reagent grade except neutral red, which was obtained from Fisher Scientific and recrystallized thrice from 50% aqueous methanol and dried under vacuum at 40°C .

RESULTS AND DISCUSSION

The linear sweep voltammetric reduction of neutral red at a

stationary mercury drop electrode exhibits partial or complete adsorption control over a wide range of conditions. For example, if the dye concentration is $1 \times 10^{-5} \text{ M}$ or less, the current remains adsorption controlled even at sweep rates as low as 5 mV/s. The voltammetric peaks conform very well to the diagnostic criteria for a fast electron transfer process under adsorption control [13]. Over several orders of magnitude the cathodic peak current is directly proportional to the sweep rate, and the peak is symmetric. The peak potentials of the anodic and cathodic peaks are equal, and provided the switching potential is sufficiently close to the cathodic peak potential, the anodic and cathodic peaks exhibit equal areas. Increasing the neutral red concentration below pH 5 causes a gradual shift toward diffusion control as indicated by decreased symmetry and a decreased dependence of the peak current on the sweep rate. Logarithmic plots of peak current vs sweep rate, such as that in Figure 1 for $1 \times 10^{-4} \text{ M}$ dye, were constructed for each dye concentration to establish the range of sweep rates which yields adsorption controlled voltammograms. As Figure 1 shows, diffusion control becomes significant at this dye concentration when the sweep rate falls below ca 0.2 V/s, but at higher sweep rates the slope of the plot is 0.96, in good agreement with the theoretical value of 1.0 for adsorption control.

Peak Potentials

Because $1 \times 10^{-5} \text{ M}$ neutral red yields voltammograms which are well defined and free of the complexities which appear at higher dye concentrations, this dye concentration was selected

for a systematic study of the effect of pH on peak morphology. Laviron has pointed out [14-18] that the peak potential, the peak width and the surface coverage are three parameters which relate directly to important aspects of the adsorption process. Since an adsorption controlled peak is symmetric, its peak potential is associated with equal surface concentrations of the oxidized and reduced forms of the electrode couple. The peak potential therefore corresponds to the formal potential of the couple in the adsorbed state [14].

Figure 2 reports the peak potentials for the reduction of neutral red from pH 2.0 to pH 9.8, and it consists of two essentially linear segments. These merge in a transition zone between pH 4 and pH 6, below which the slope is -90 mV/pH and above which it is -59 mV/ph . That is, below pH 4, the reduction of neutral red is a 3-proton, 2-electron process whereas above pH 6 it is a 2-proton, 2-electron process. Qualitatively, these peak potentials agree reasonably well with the formal potentials determined potentiometrically by Nikolskii et al [5,6], but there are some notable differences. It is not surprising that the peak potential-pH plot does not reveal the 1-proton, 2-electron process observed potentiometrically between pH 6.4 and pH 6.6. This simply reflects the fact that the voltammetric peak potentials lack the precision necessary for discrimination of such fine detail. More significant is the fact that the peak potentials are consistently more negative than the potentiometric values and the magnitude of the difference increases with increasing pH. At pH 4, the difference is 20 mV whereas at pH 9.5, the difference

is 60 mV. This difference must arise in part at least because the voltammetric peak potentials reflect the formal potential of the surface couple whereas the potentiometric measurements reflect the formal potential of the bulk couple. As was pointed out by Laviron [14], the formal potential of the surface couple is offset from the formal potential of the bulk couple by a term which represents the difference between the standard free energies of adsorption of O and R. Thus, if, as in the present situation, the peak potential is more negative than the formal potential of the bulk couple, O is adsorbed more strongly than R. Because the peak potential and the equilibrium potentials were measured under somewhat different conditions, quantitative evaluation of the adsorption energy term from these data is not possible. On the other hand, the systematic increase in the magnitude of this difference between the formal potential of the bulk couple and the formal potential of the surface couple with increasing pH suggests that the adsorption free energy term becomes more important at higher pH. A number of other aspects of the voltammograms which support this premise will be discussed in later sections.

Surface Coverage of Acidic Neutral Red

Below ca pH 4.5 the surface coverage of neutral red increases steadily with increasing bulk concentration of dye. Typical of the adsorption in such solutions is the isotherm in Figure 3, which refers to pH 3.0. This pH is 3.6 units below the pK_a of neutral red [6], so that the species undergoing adsorption is without doubt the cationic conjugate acid of the dye, DH^+ . The

isotherm bears little resemblance to the Langmuir isotherm or to any of the other isotherms often encountered in electrochemistry, and it exhibits two features which merit particular attention.

First, as the dye concentration falls below the 10^{-6} M level, the surface coverage approaches a lower limiting value of $24 \mu\text{C cm}^{-2}$, which corresponds reasonably well to monolayer coverage in which the dye molecules are closely packed with the plane of the heterocyclic rings parallel to the electrode surface. The surface area occupied per molecule is 130 \AA^2 , which agrees fairly well with the cross section area of 120 \AA^2 reported for methylene blue [9-11], the dimensions of which must be similar to those of neutral red. The persistence of monolayer coverage at bulk concentrations below 10^{-6} M demonstrates the strong adsorption of neutral red on mercury. We have been unable to study the submonolayer adsorption of neutral red because at the submicromolar bulk concentrations that are necessary it is difficult to obtain reproducible coverage.

The second important aspect of the adsorption of the acidic form of neutral red is that for bulk concentrations from 2×10^{-7} to $3 \times 10^{-4} \text{ M}$, the surface coverage is directly proportional to the degree of aggregation on the bulk concentration as estimated from the equilibrium constants reported by Nikolskii et al [5-7]. In Figure 3, the vertical scale of the plot of the degree of aggregation is adjusted so that the lower limit, i.e., the point corresponding to monomeric dye, coincides with the lower limit of the surface coverage plot, i.e., the point corres-

ponding to monolayer coverage. Over the 3 decades of dye concentration studied, the correlation of the surface coverage with the degree of aggregation is quite satisfactory, meaning that to a good approximation, the adsorption can be envisioned as the concurrent adsorption of the monomer, the dimer and the tetramer of neutral red. All three are adsorbed equally strongly in that there is no evidence that the magnitude of the adsorption equilibrium constant depends on the degree of aggregation of the bulk dye. The extent of adsorption of acidic neutral red increases monotonically with increasing bulk concentration, with no discontinuities which indicate the formation of distinguishable phases. That is, for surface coverages of acidic neutral red that range from one monolayer to three, the coverage is formally equivalent to a monolayer of aggregated dye.

To further test the influence of the aggregation of neutral red on the extent to which it is adsorbed, we have determined its adsorption isotherm at pH 3.0 in 50% aqueous methanol. The visible spectrum of the dye shows that under these conditions aggregation is virtually absent over the concentration range of interest so that the bulk species is monomeric DH^+ . Figure 4 reports the isotherm, which differs substantially from the isotherm for aqueous solutions in Figure 3. Relative to the extent of adsorption from aqueous solution, the extent of adsorption from 50% methanol is markedly lower, but the most striking feature of the adsorption process in 50% methanol medium is that the isotherm displays an upper limiting coverage of $25 \mu C \text{ cm}^{-2}$, which corresponds to essentially one monolayer. This result

indirectly supports the proposal of a monolayer of aggregated dye particles in that it demonstrates that formation of a monolayer of the monomeric dye is a limiting case.

Surface Coverage of Basic Neutral Red

Above pH 8.5 the adsorption isotherm of neutral red exhibits an abrupt increase in surface coverage when the bulk concentration exceeds a critical value. The isotherm at pH 9.5, which is reported in Figure 5, typifies the behavior of neutral red in alkaline solution. At pH 9.5 ca 99.8% of the dye in solution is converted to the uncharged conjugate base D, so that it is clear that this is the species undergoing adsorption. Provided the bulk concentration of the dye is below $1 \times 10^{-5} \text{ M}$, the coverage increases slowly with increasing bulk concentration, but when the bulk concentration exceeds this value, the surface coverage rises abruptly. The equilibrium solubility of neutral red under these conditions as estimated spectrophotometrically is $5.0 \times 10^{-6} \text{ M}$, a value just below the knee of the curve. Concentrations of basic neutral as much as sixfold higher than the equilibrium solubility are readily prepared by raising the pH of a solution of the much more soluble acidic form of the dye, and once prepared, they are stable for several hours. During this time they show no sign of precipitation and their voltammetric behavior does not change perceptibly. By analogy to the adsorption behavior of acidic neutral red, we attribute the sharp increase in surface coverage of basic neutral red which occurs on exceeding the equilibrium solubility to the formation of aggregates. It is interesting that the abrupt increase in surface coverage occurs when the coverage exceeds $50 \text{ } \mu\text{C cm}^{-2}$ or

approximately two monolayers, but we do not know whether this result has the same significance as the coverages observed in acidic solution. It is also not fully clear how these results relate to those of Nikolskii et al [5,6], who concluded that even when the dye concentration is as high as $5 \times 10^{-5} \text{ M}$, the basic form of neutral red does not form aggregates. In their studies, the bulk solution contained both neutral red and leuco neutral red in equal concentration, and interaction of basic neutral red with leuco dye may have suppressed its aggregation.

Peak Morphology

Both the bulk concentration of the dye and the pH strongly affect the morphology of the adsorption controlled voltammetric peak of neutral red. These changes in peak shape are manifestations of the attractive and repulsive interactions between adsorbed molecules, which can be substantial at high surface coverage. Of the formal methods for the analysis of such interactions in linear sweep voltammetry, that developed by Laviron [14-18] is particularly useful. In his analysis of adsorbate interactions, Laviron considers three distinct types of adsorbate interactions: those between molecules of adsorbed O, those between molecules of adsorbed R and those of molecules of adsorbed O with molecules of adsorbed R. These three interactions are denoted respectively by the terms a_O , a_R , and a_{OR} , which are positive if the interaction is attractive and negative if it is repulsive, and they are taken into account by assuming that a Frumkin isotherm is obeyed. The important result here is that these interactions influence the shape of an adsorption controlled voltammetric peak and cause it

to deviate from that of an ideal peak governed by a Langmuir isotherm. This deviation is governed by the magnitude of the quantity $Gv\theta_T$, where the definition of G in terms of a_O , a_R , and a_{OR} is given by Eqn. 1, θ_T is the ratio of coverage of O plus R to the

$$G = a_O + a_R - 2a_{OR} \quad (1)$$

maximum possible coverage and v is the (usually unknown) quantity of solvent displaced by the adsorption of O or R. If the value of $Gv\theta_T$ is essentially zero, as is true either when the surface coverage approaches zero or when the value of G itself is zero, the peak has the same shape as an ideal peak, i.e., one governed by the Langmuir isotherm. This does not mean that intermolecular interactions are unimportant, but simply that the algebraic sum of the interaction terms is zero. A negative value of G causes the peak to be broader and lower than the ideal peak whereas values of G between zero and two cause the peak to be narrower and higher than the ideal peak. Because the value of v for adsorption of neutral red is not known, we can only apply the theory qualitatively, but despite this constraint, it provides very useful insights concerning the nature of the intermolecular interactions in adsorbed neutral red and the manner in which they depend on the bulk concentration and the degree of protonation of the dye.

The effect of pH on the shape of the neutral red voltammogram is simplest if the dye concentration is $10^{-5}M$ or less. For such low bulk concentrations, the peak width depends in a simple and characteristic manner on pH as shown by the data in Figure 6. Increasing the pH from 4 to 6 causes the peak width to fall from

85 mV to 45 mV, the theoretical value for an ideal peak. That is, below pH 4 the value of G is negative, consistent with a net repulsive interaction between the adsorbed molecules, whereas above pH 6 it is zero, consistent with no net interaction between the adsorbed molecules.

The most striking feature of this transition is that although its shape suggests that it arises from a one proton dissociation reaction of either neutral red or the leuco dye, it does not coincide with a pK_a of either species. Rather, the midpoint of this transition falls at pH 5.2, approximately midway between the pK_a s of the leuco dye (4.4 and 6.4) and more than a full pH unit below the pK_a of neutral red (6.6)[6,7].

Although we cannot completely define the cause for the increase in the value of G with increasing pH, we can partially resolve the question by considering the pH dependences of the charges of neutral red and leuco neutral red and the effects these charges would exert on a_O , a_R and a_{OR} in Eqn. 1. The pK_a of neutral red is 6.6, while the pK_a s of leuco neutral red are 4.4 and 6.4 [6,7], so that the pH dependences of the charges of the two species can be summarized as follows. Below pH 4.4, neutral red exists as the univalent cation DH^+ , while leuco neutral red exists as the divalent cation DH_4^{+2} . Between pH 4.4 and pH 6.4, both neutral red and the leuco dye exist as the univalent cations DH^+ and DH_3^+ . The leuco dye is converted to the neutral species DH_2 above pH 6.4 and neutral red is converted to the neutral species D above pH 6.6. In principle, the pH dependence of the value of G is consistent with either an increase

in the value of a_O or a_R or a decrease in the value of a_{OR} , but the latter possibility appears extremely unlikely. For a_{OR} to decrease would require that the interaction between neutral red and leuco neutral red become less attractive as the pH increases. However, since the positive charges of both neutral red and the leuco dye decrease with increasing pH it is difficult to envision that the interaction of these two species becomes less attractive with increasing pH. On the other hand, an increase in a_O or an increase in a_R , or both, is consistent with the pH dependences of the charges of neutral red and leuco neutral red. Since both a_O and a_R influence G in the same way, we are unable to determine whether the increase in the value of G arises from an increase in a_O , an increase in a_R or an increase in both. In principle, one could distinguish between an increase in a_O and an increase in a_R over a given pH range by monitoring the change in surface coverage, which is sensitive only to the adsorption characteristics of neutral red. The surface coverage does appear to be pH dependent, but the change is not sufficiently greater than the uncertainty in our measurement to permit us to draw clear conclusions. Between pH 2.2 and pH 4.8, the surface coverage of a $1 \times 10^{-5} M$ dye solution averages $32 \mu C/cm^2$, and with further increase in pH the coverage rises until it reaches a value of ca $42 \mu C/cm^2$ at pH 7. These measurements have an uncertainty of ca 10%, so that the transition is poorly defined and correlation with peak width data must await more precise coverage measurements.

Despite the inability to determine whether the increase in the value of G between pH 4 and pH 6 arises from an increase in

a_O or a_R , it is clear that the $pK_a(s)$ responsible must be greater than 6. The reason for this is that if an attractive interaction preferentially affects the conjugate base of an acid-base pair, it lowers the free energy of the base, thus increasing the acid dissociation constant and lowering the pK_a . Although this fact does not establish whether neutral red ($pK_a 6.6$) or leuco neutral red ($pK_a 6.4$) causes the increase in G , it draws attention to an important point. The increase in G centered at pH 5.2 corresponds to a surface pK_a , and regardless of whether the species involved is neutral red or leuco neutral red, the surface pK_a is more than 1 unit smaller than the bulk pK_a . Adsorption clearly changes the acid-base behavior of neutral red significantly with respect to the behavior in bulk solution and full understanding of the behavior of the adsorbed dye will require determination of its surface pK_a s.

That this systematic increase in the net value of G with increasing pH observed with $10^{-5}M$ neutral red does indeed result from an increase in either a_O or a_R (or both) is confirmed by the pH dependence of voltammograms of more concentrated dye. Typical of such behavior is the progressive splitting of the peak of slow voltammetric sweeps of $2 \times 10^{-4}M$ dye reported in Figure 7. Below pH 5 there is only a single rather broad peak, the asymmetry of which indicates a significant diffusion contribution to the current. At pH 5 the peak increases significantly in height and, in contrast to the featureless envelope seen at lower pH, the peak exhibits a distinct shoulder on its rising edge. Further increase in pH causes progressive change in peak morphology that leads

ultimately to the appearance of the two extremely sharp closely spaced peaks seen at pH 6.36.

The influence on the peak potentials of pH and the dye concentration demonstrates clearly that the less cathodic of the two peaks corresponds to the single peak which characterizes the voltammograms of 10^{-5}M neutral red, and that the more cathodic peak represents the electroreduction of neutral red by a process which is electrochemically distinguishable from the first. Figure 8, which reports the pH dependences of the two reduction peaks, shows that from approximately pH 5.2, where peak splitting is first apparent to approximately pH 6.6, the two peaks are separated by 40 mV. The solid line in Figure 8, which is the pH-potential plot for the single peak displayed by voltammograms of 10^{-5}M neutral red, shows clearly that the potential of the less cathodic peak in the voltammograms of $2 \times 10^{-4}\text{M}$ neutral red corresponds closely to the potential of the single peak in the voltammograms of $1 \times 10^{-5}\text{M}$ dye. Additional support for this assignment is found in Figure 9, which shows how the number and the potential of voltammetric peaks at pH 5.44 depend on the neutral red concentration. If the dye concentration is $2 \times 10^{-5}\text{M}$ or lower, the voltammogram displays only a single peak, but if the dye concentration is $5 \times 10^{-5}\text{M}$ or higher, the voltammogram exhibits two peaks. In agreement with Figure 8, Figure 9 shows clearly that the potential of the less cathodic of the two peaks corresponds to the potential of the single peak of the voltammogram of the 10^{-5}M solution. The information in Figures 8 and 9 establishes that the voltammetric peak which appears and grows pro-

gressively as the dye concentration is increased above $2 \times 10^{-5} \text{ M}$ represents a new pathway for the reduction of neutral red that is energetically distinguishable from the reduction pathway at lower concentration.

Adsorbate Phases

Although the existence of the two voltammetric peaks when the surface coverage is high demonstrates that there are two energetically distinguishable pathways for reduction of neutral red, it does not indicate why the two pathways differ in energy by a small but significant degree. The answer to this question is found in the nature of the adsorption isotherm of neutral red in the pH range which yields voltammograms with doublet peaks. Figure 10, which reports the isotherm at pH 5.60, shows that raising the bulk concentration of dye from $3 \times 10^{-7} \text{ M}$ to $3 \times 10^{-4} \text{ M}$ causes the surface coverage to rise from one monolayer to three monolayers, i.e., to trilayer coverage. It is particularly significant that most of this change in surface coverage occurs over a very small range of bulk concentrations. Increasing the bulk concentration of neutral red from $2 \times 10^{-5} \text{ M}$ to $5 \times 10^{-5} \text{ M}$ causes the surface coverage to increase from $30 \text{ } \mu\text{C}/\text{cm}^2$, which corresponds to slightly more than monolayer coverage, to $70 \text{ } \mu\text{C}/\text{cm}^2$, which corresponds to nearly three monolayer coverage. Evidently, surface coverages of a monolayer or slightly more correspond to one preferred state of the surface, and surface coverages of three monolayers or slightly less correspond to a second preferred state. Of even more significance than the precise levels of surface coverage is the fact that the attainment of the higher

level coverage coincides with the onset of voltammetric peak splitting. The arrow in Figure 10 indicates the first evidence of peak splitting, and it corresponds to the upper end of the sharp increase in surface coverage. When the surface coverage reaches $72 \mu\text{C}/\text{cm}^2$ the voltammogram exhibits two very well defined and distinct peaks.

Although the transition in the surface coverage-concentration plot for neutral red is somewhat less well defined than the extremely sharp transitions observed by Murray [19-21] in the anion induced adsorption of heavy metals, there is little doubt that it arises from the same phenomenon. The close correlation between the appearance of the second voltammetric peak and the attainment of the limiting trilayer surface coverage shows that the abrupt increase in surface coverage does indeed represent formation of a new adsorbate phase. Perhaps the most striking aspect of the formation of the second adsorbate phase is that it has such a small effect on the energetics of the reduction of neutral red. The two peak potentials differ by only 40 mV, which suggests that coincident with the formation of the new phase of the oxidized species of neutral red there is also the formation of a new phase of the reduced species, which nearly offsets the change in the free energy of the oxidized species. That is, in the surface environment characteristic of trilayer surface coverage, the free energies of both neutral red and leuco neutral red are shifted by almost the same extent relative to their free energies in the surface environment characteristic of monolayer coverage.

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REFERENCES

1. E. Witt, Ber. Dtsch. Chem. Ges., 12(1978)931.
2. W.M. Clark and M.E. Perkins, J. Am. Chem. Soc., 54(1932)1228.
3. P. Bartels, Z. Physik. Chem. N.F. (Frankfurt), 9(1956)74.
4. P. Bartels, Z. Physik. Chem. N.F. (Frankfurt), 9(1956)95.
5. B.P. Nikolskii, V.V. Palchevskii, L.A. Polyanskaya and V.V. Boriskin, Dokl. Akad. Nauk SSSR, 193(1970)352.
6. B.P. Nikolskii, V.V. Palchevskii, L.A. Polyanskaya and A.G. Rodichev, Dokl. Akad. Nauk SSSR, 194(1970)1334.
7. B.P. Nikolskii, B.B. Palchevskii, L.A. Polyanskaya, N.P. Kiseleva and G.F. Pustarnakova, Dokl. Akad. Nauk SSSR, 196(1971)1365.
8. M. Suzuki and S. Sawada, Denki Kagaku, 39(1979)249.
9. J.M. Los and C.K. Tomkins, Can. J. Chem., 37(1959)315.
10. S. Roffia and G. Feroci, J. Electroanal. Chem. Interfacial Electrochem., 41(1973)367.
11. F. Pergola, G. Piccardi and R. Guildelli, J. Electroanal. Chem. Interfacial Electrochem., 83(1977)33.
12. G. Papeschi, M. Costa and S. Bordi, J. Electrochem Soc., 128(1981)1518.
13. R.S. Nicholson and I. Shain, Anal. Chem., 36(1964)706.
14. E. Laviron, Bull. Soc. Chim. Fr., (1967)3717.
15. E. Laviron, J. Electroanal. Chem. Interfacial Electrochem., 52(1974)395.
16. E. Laviron, J. Electroanal. Chem. Interfacial Electrochem. 63(1975)245.
17. E. Laviron, J. Electroanal. Chem. Interfacial Electrochem., 100(1979)263.
18. E. Laviron, J. Electroanal. Chem. Interfacial Electrochem., 105(1979)25.
19. C.M. Elliott and R.W. Murray, J. Am. Chem. Soc., 96(1974)3321.
20. H.B. Herman, R.L. McNeely, R. Surana, C.M. Elliott, and R.W. Murray, Anal. Chem., 46(1974)1258.
21. C.M. Elliott and R.W. Murray, Anal. Chem., 48(1976)259.

FIGURE CAPTIONS

- Figure 1 Dependence of peak current on sweep rate for cathodic peak of $1 \times 10^{-4} \text{ M}$ neutral red at pH 2.74.
- Figure 2 Peak potential -pH plot for $1 \times 10^{-5} \text{ M}$ neutral red at a sweep rate of 100 mV/s
- Figure 3 Adsorption isotherm of neutral red in aqueous 0.1M KCl solution at pH 3.0. The scale defining the degree of aggregation is normalized so that a degree of aggregation of 1.0 corresponds to a surface coverage of $24 \mu\text{C}/\text{cm}^2$ (1 monolayer)
- Figure 4 Adsorption isotherm of neutral red in 50% methanolic 0.1M KCl solution at pH 3.0.
- Figure 5 Adsorption isotherm of neutral red in aqueous 0.1M KCl at pH 9.54. The solubility of the dye under these conditions is ca $5 \times 10^{-6} \text{ M}$
- Figure 6 Effect of pH on the width at half height of the cathodic peak of neutral red. The dye concentration is $1 \times 10^{-5} \text{ M}$ and the sweep rate is 100 mV/s.
- Figure 7 Voltammograms of $2 \times 10^{-4} \text{ M}$ neutral red showing progressive peak splitting with increasing pH. The sweep rate is 100 mV/s.
- Figure 8 Peak potential - pH plot for $2 \times 10^{-4} \text{ M}$ neutral red showing the appearance of the second peak. The solid line is the peak potential-pH plot for the single peak observed for $1 \times 10^{-5} \text{ M}$ dye.

Figure 9

The influence of concentration on the number and the potential of the voltammetric peak(s) of neutral red at pH 5.44.

Figure 10

Adsorption isotherm of neutral red in aqueous 0.1M KCl at pH 5.60. The arrow indicates the onset of peak splitting in the slow sweep voltammograms.

Figure 1

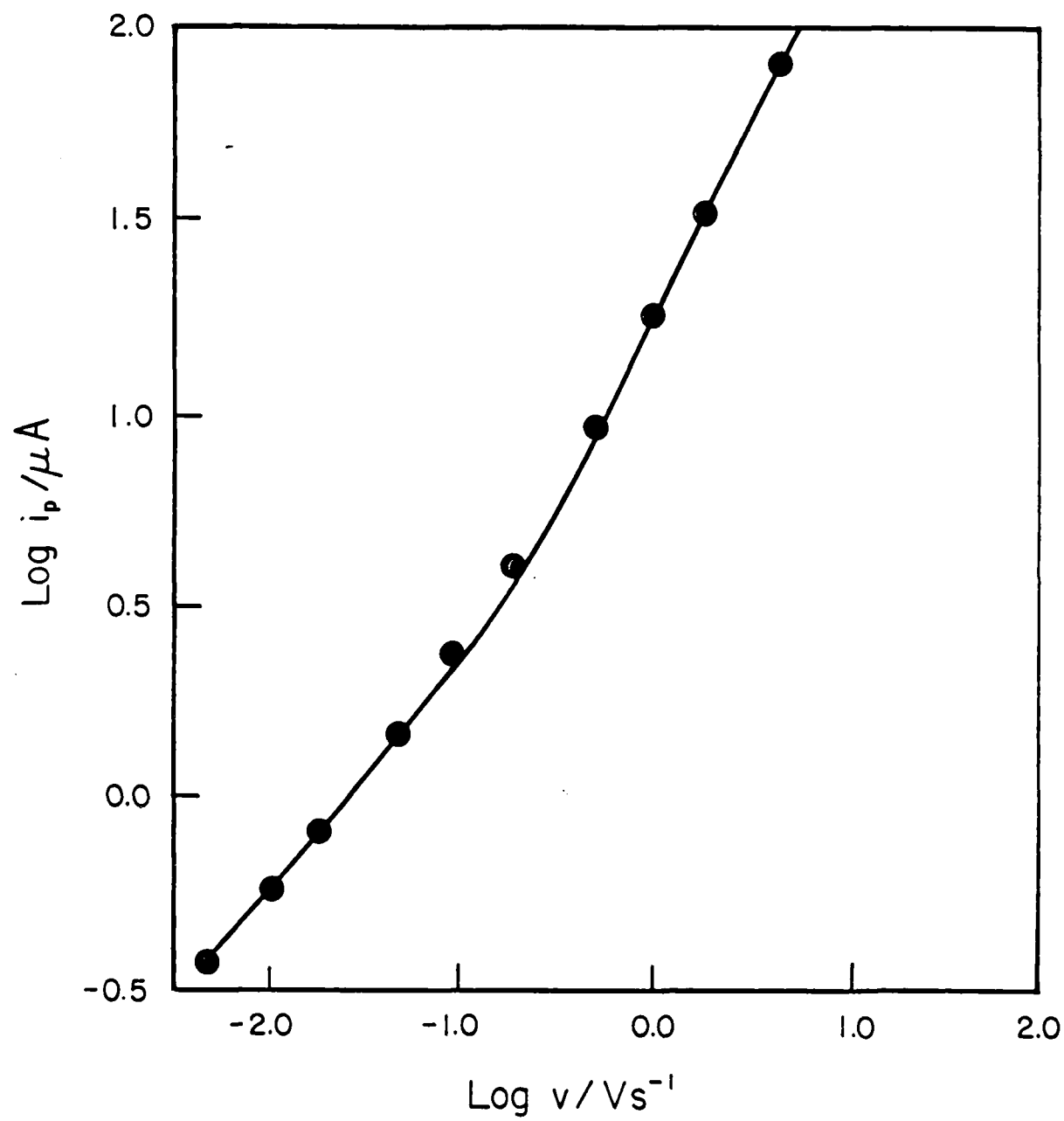


Figure 2

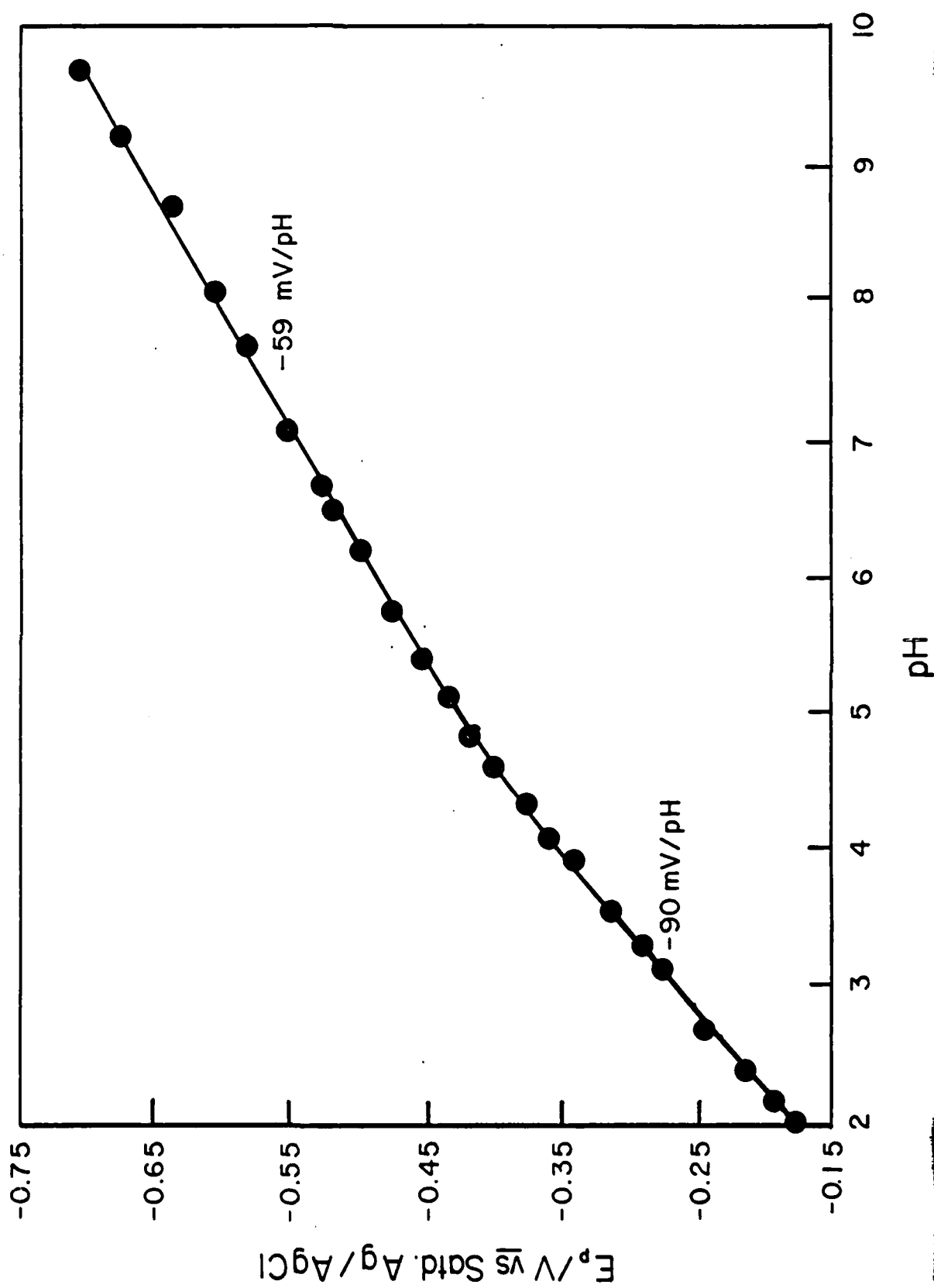


Figure 3

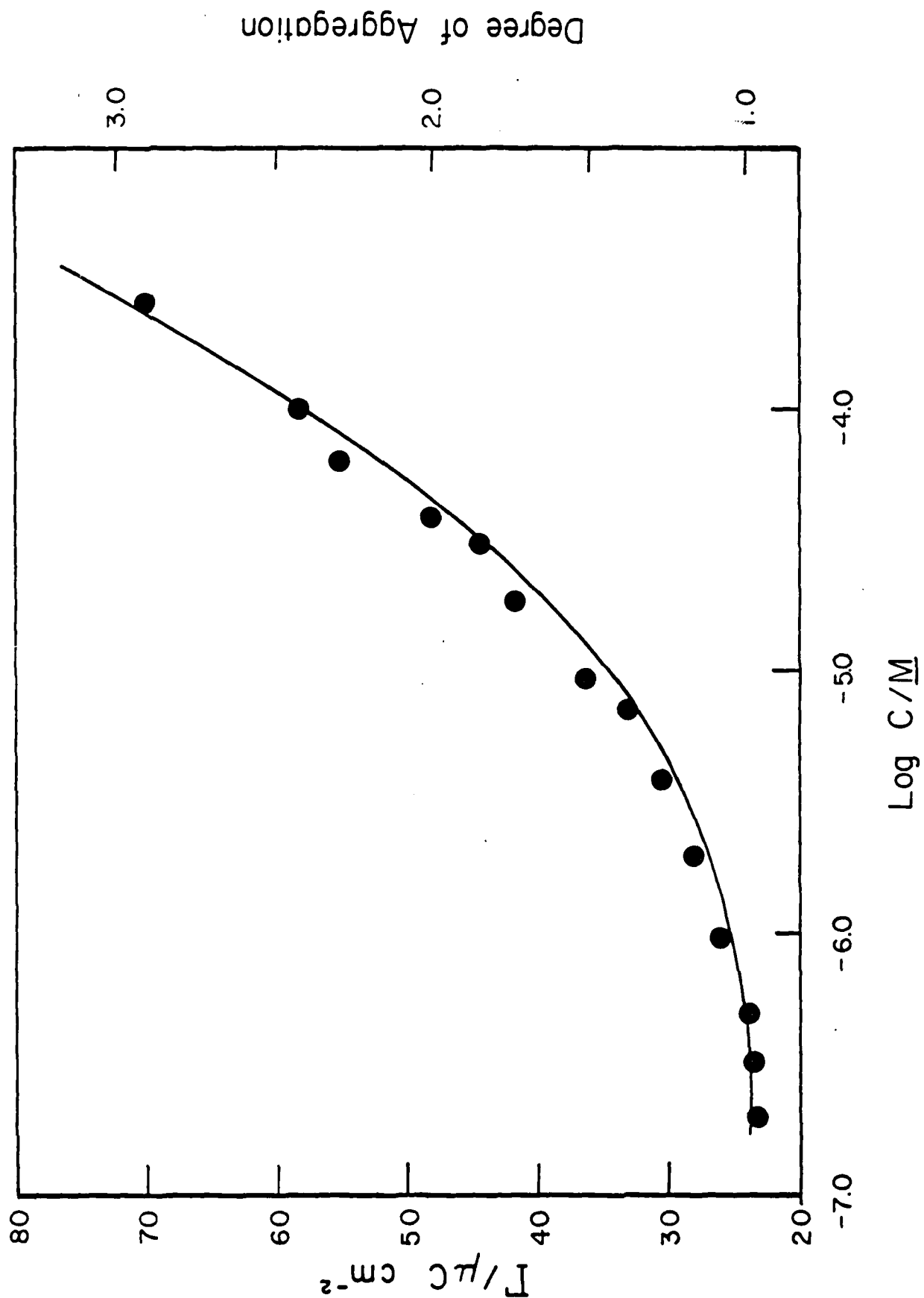


Figure 4

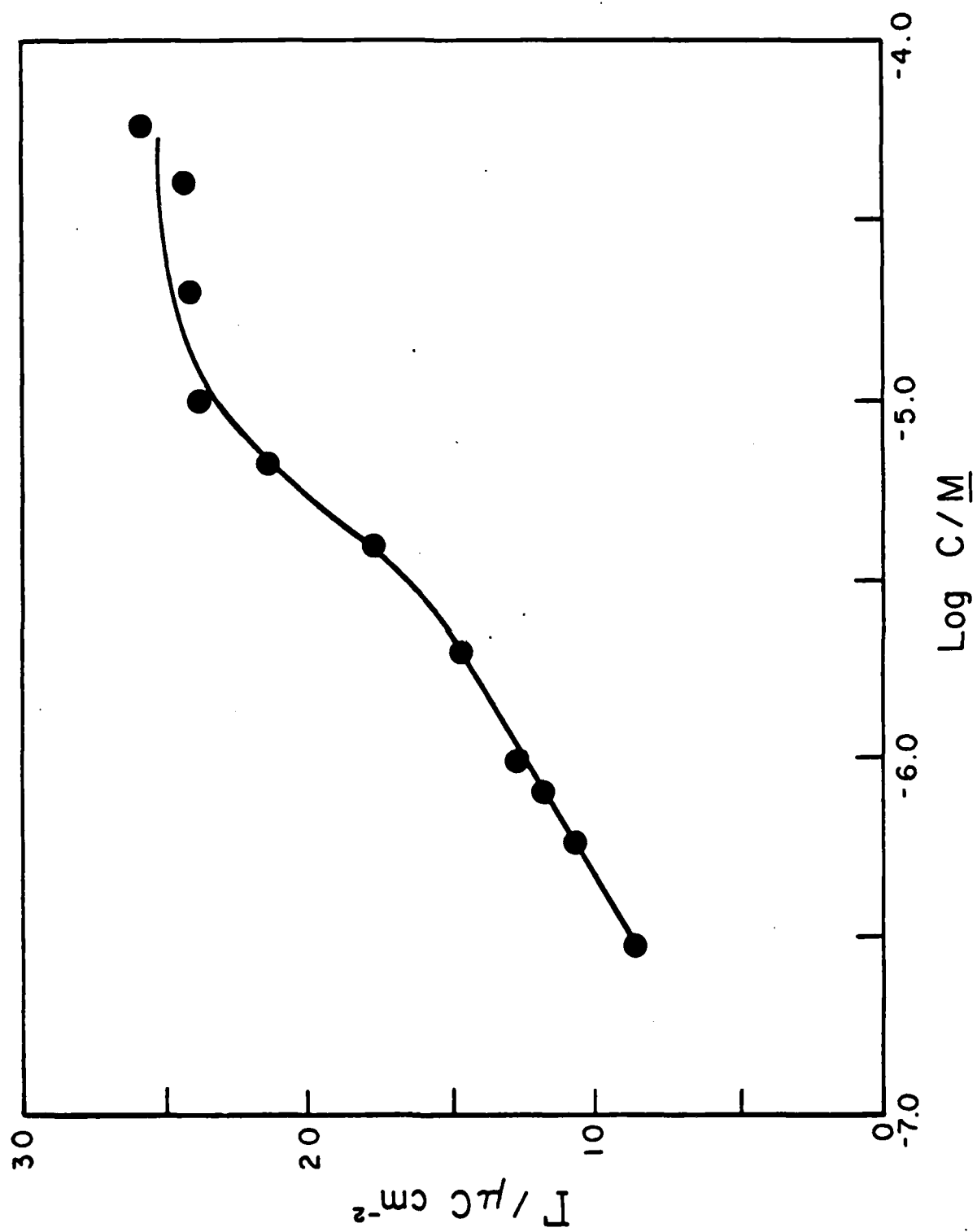


Figure 5

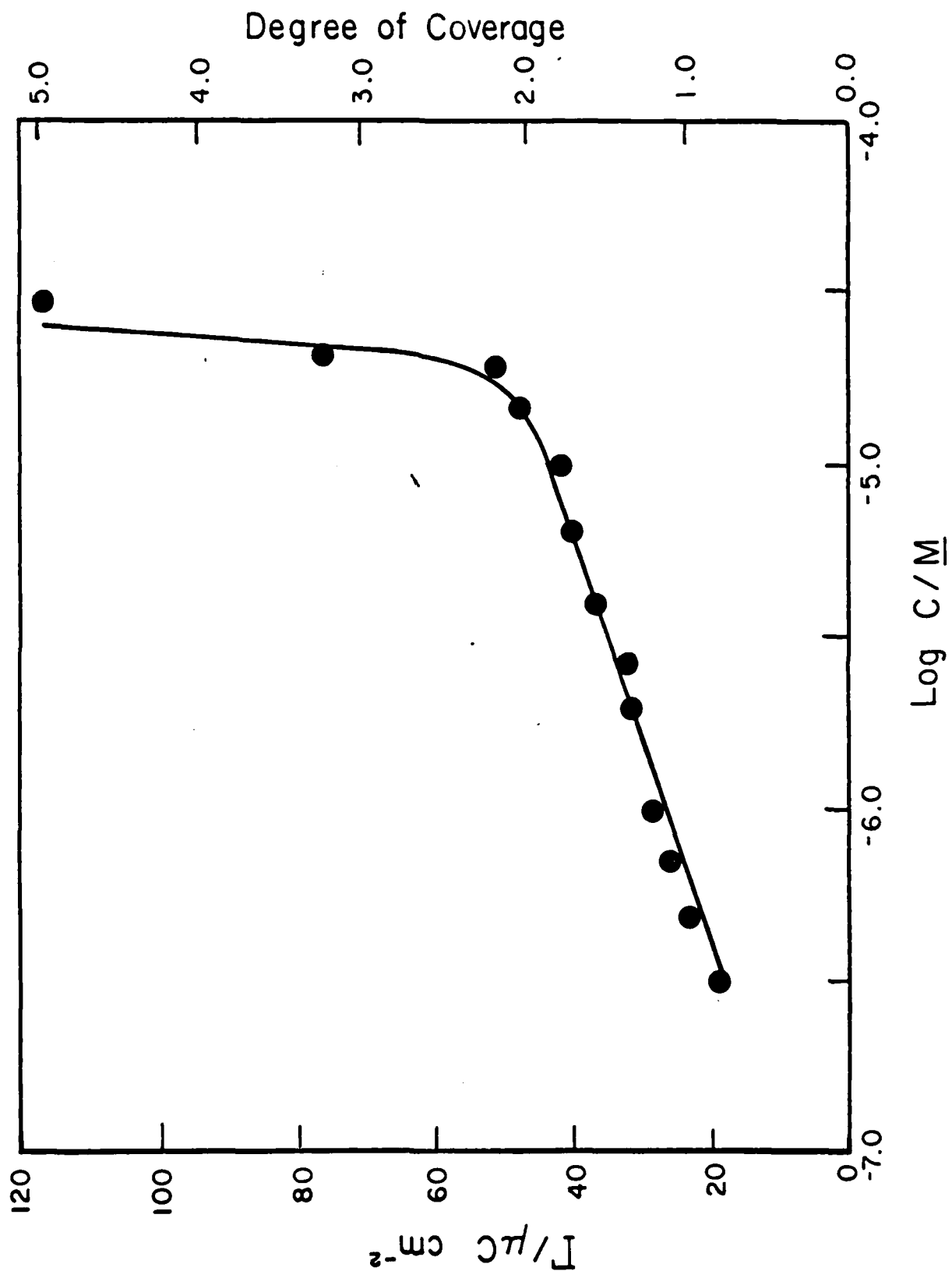


Figure 6

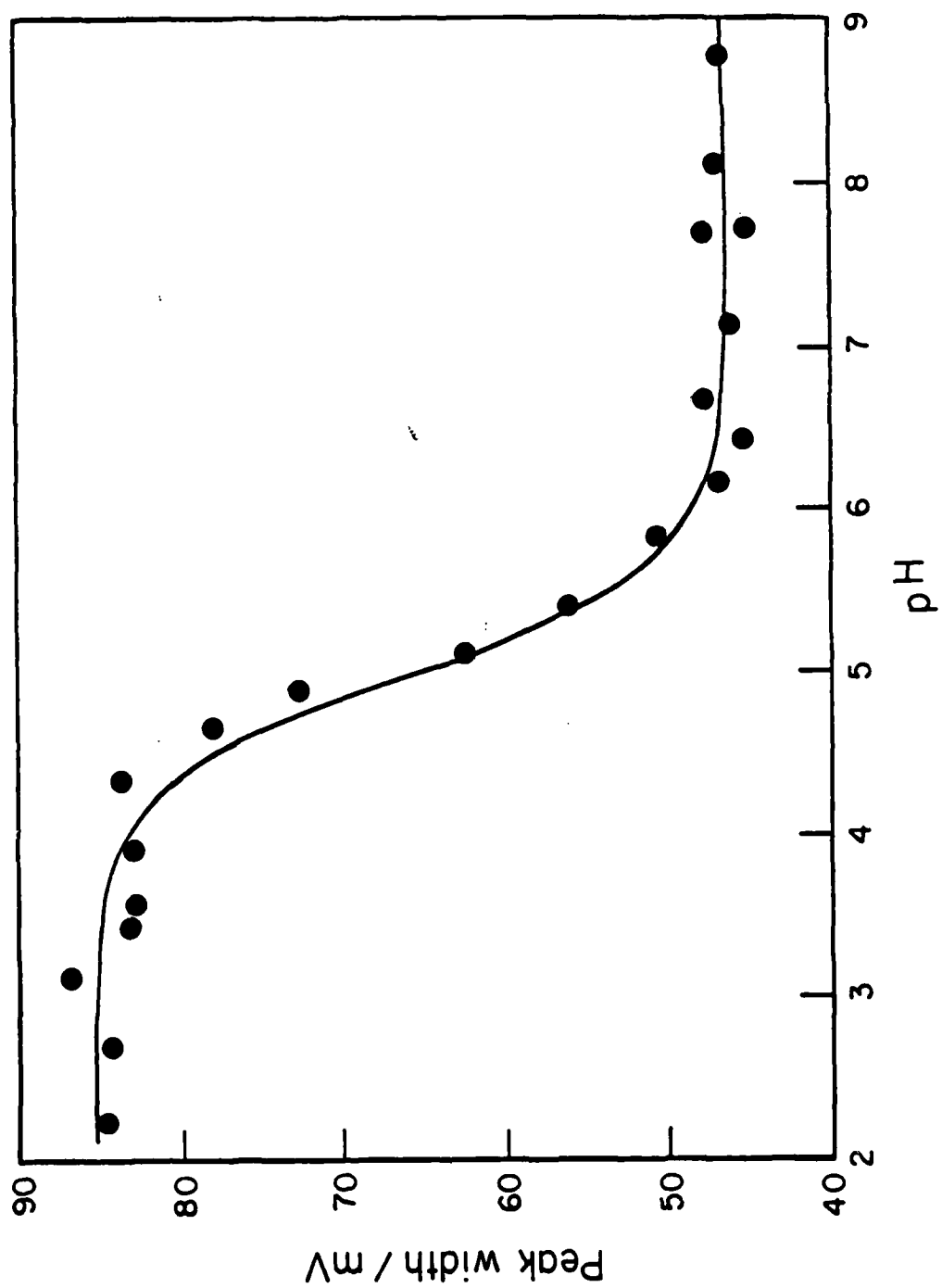


Figure 7

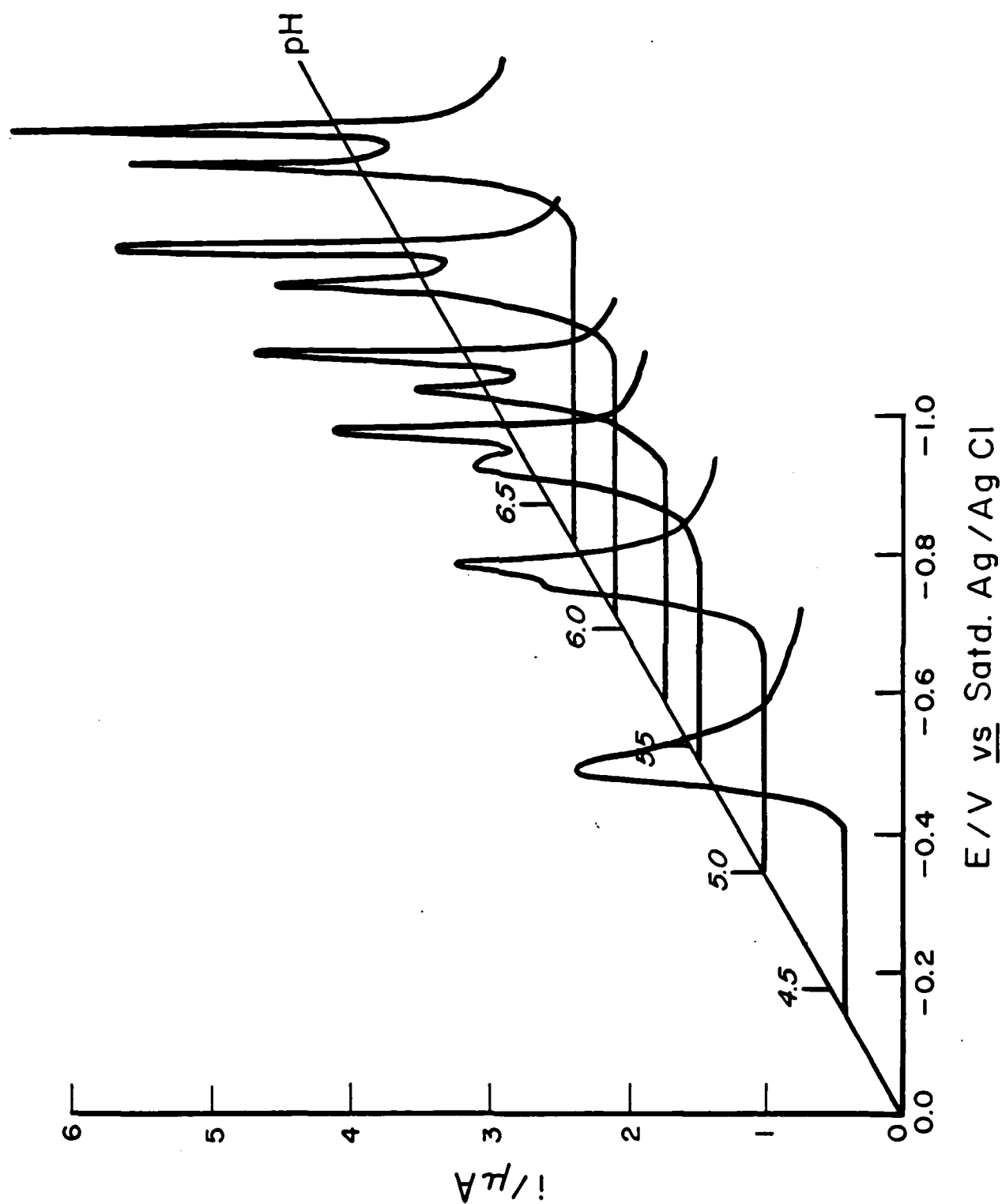


Figure 8

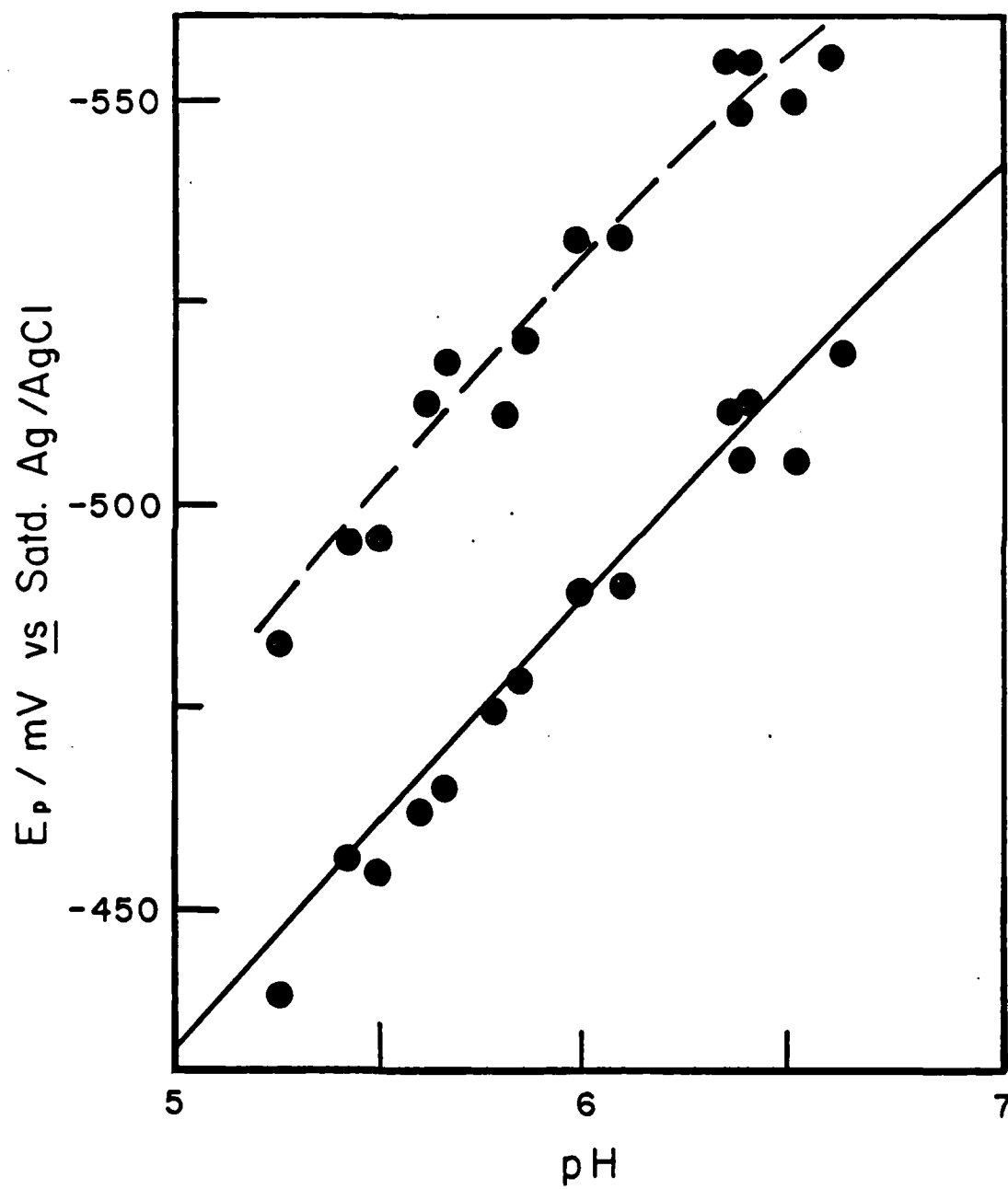


Figure 9

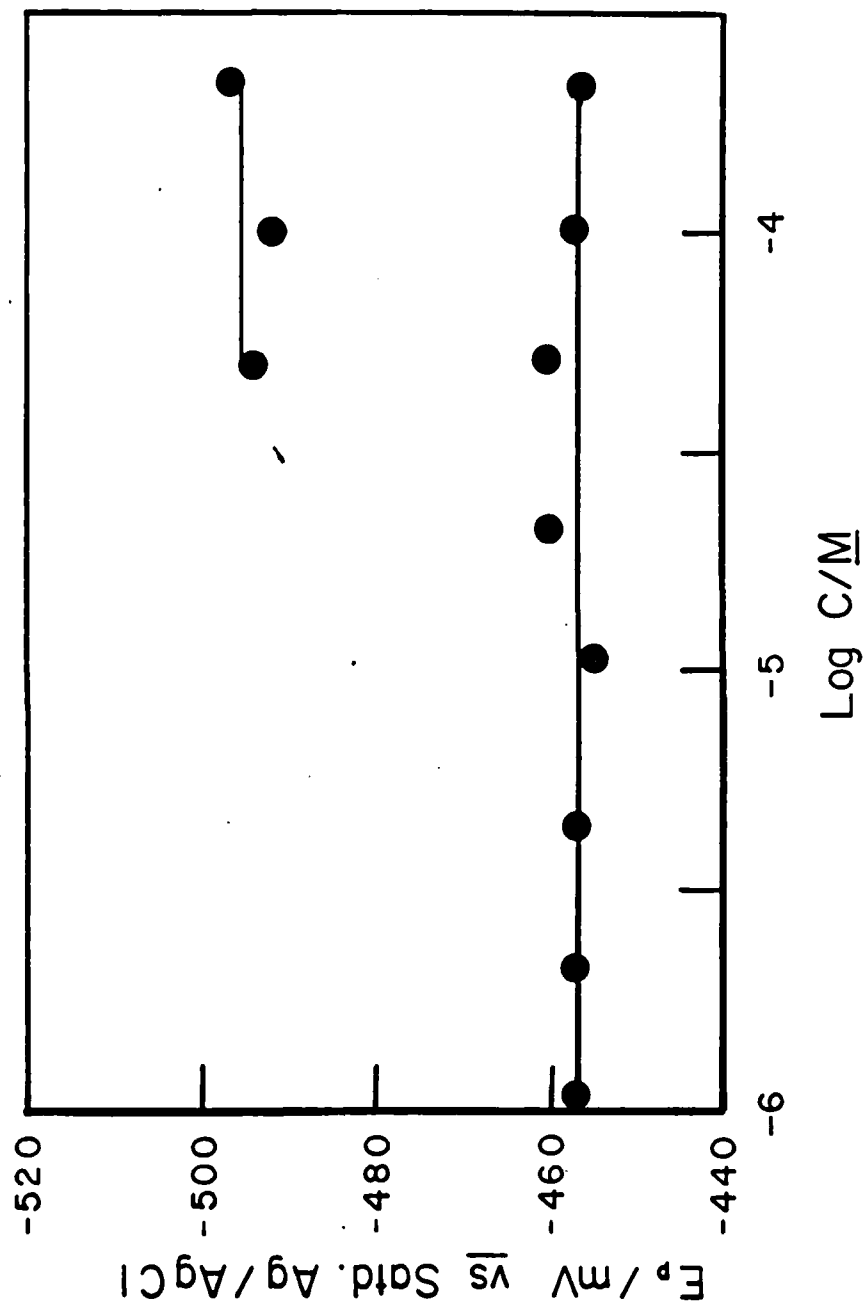
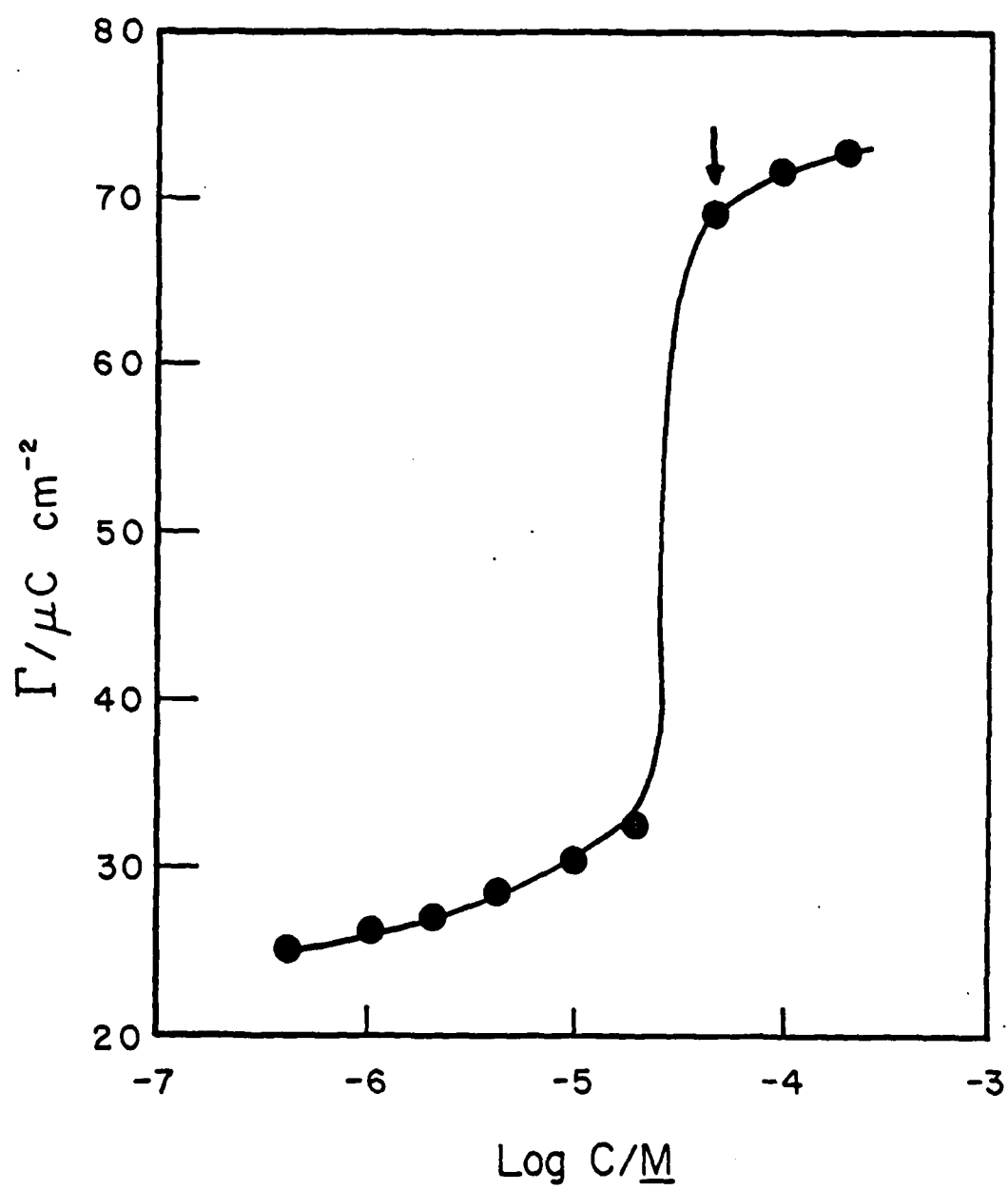


Figure 10



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